[Second Edition.]

PATENT SPECIFICATION

Application Date: April 8, 1933. No. 10,536/33. 419,445

Complete Specification Left: Feb. 27, 1934.

Complete Specification Accepted: Nov. 8, 1934.

PROVISIONAL SPECIFICATION.

Improvements in and relating to the Manufacture of Coloured Moulding Compositions.

We, HAROLD CLAYTON, of 12, Broadway Avenue, Cheadle, in the County of Chester, and HARRY JONES, of 9, Vale Street, Heywood, near Manchester, in the County of Lancaster, both British Subjects, do hereby declare the nature of this invention to be as follows :—

This invention relates to improvements in the manufacture of coloured moulding compositions and in fillers therefor and moulded articles thereof.

It is customary in the manufacture of moulded articles to prepare a moulding composition comprising a mixture of a plastic, generally a synthetic plastic, and a filler and then to form shaped articles therefrom by moulding in a press preferably at an elevated temperature. Coloured articles are generally made by mixing with the plastic a proportion of finely divided pigment or other colouring matter during or after the incorporation of the filler. It has been proposed to produce a moulding material composed of woven fabric impregnated with a fusible resinous binder and subdivided into substantially dry flakes of such size (e.g. from $\frac{1}{8}$ to $1\frac{1}{2}$ inches long by from $\frac{1}{8}$ to $1\frac{1}{2}$ inches wide) small enough to permit the moulding composition to flow in a mould under the influence of heat and pressure and large enough substantially to prevent the flakes sticking together in irregular masses after impregnation; it was also suggested to produce striking effects by dyeing part or all of the fabric pieces with various colours or by including pigments in the composition.

It has now been found that improved results can be obtained in the manufacture of moulded articles from plastics, preferably synthetic plastics, by dyeing or otherwise colouring the filler from an aqueous medium preferably before mixing it with the plastic.

By the expression "filler" we mean an organic or inorganic substance of fibrous or cellular structure characterised by the requisite degree of subdivision and capable of retaining a colouring agent which is applied thereto. The expression does not, however, include subdivided woven fabric. The degree of subdivision is of the order of one twenty-fifth to one hundred and fiftieth of an inch. Examples of such substances are wood flour, wood meals, wood pulp and asbestos which are customarily employed in moulding compositions. Preferably they are sufficiently finely divided to pass a 60-mesh sieve. The colouring agent which is applied to the filler may be retained owing to the affinity, physical or chemical, of the filler therefor, or alternatively the colouring agent may be simply deposited or formed upon or within the filler.

The plastic may be of the thermo-setting type such as an intermediate condensation product of a phenol-fromaldehyde, urea-formaldehyde, thiourea-formaldehyde, coumarone or the like resin, or it may be of the thermo-plastic type such as a vinyl resin (including styrol resins) or a cellulose ester or other composition or a mixture of these.

The dyeing or colouring of the filler from an aqueous medium results in important advantages in practice and increases the range of colouring matters which it is possible to employ. Many direct cotton colours, sulphur dyes, vat dyes and the like which it is difficult or impossible to use, at any rate with good result, by the customary methods of incorporation may be employed. Some of these, owing to their fastness to light, heat, acid and the like, form extremely valuable colouring matters to employ in moulded articles. Moreover, by dyeing or colouring the filler itself darker shades are as a rule obtained than when an equal amount of the colouring matter is simply mixed with the filler and plastic. A valuable economy is thus often secured in addition to an improved result.

According to the present invention, in the manufacture of moulding compositions or moulded articles, the filler is dyed or otherwise coloured from an aqueous medium preferably prior to its incorporation with the plastic. The dyeing or colouring may take place, however, during or after the incorporation with the plastic provided that it is effected before the plastic has had an opportunity of per-

meating and penetrating the filler to such an extent as to render it incapable of being penetrated by an aqueous medium. The use of wetting-out agents is of importance in the dyeing or colouring of the filler although not essential for success. The invention includes the process of making a filler for incorporation with a plastic, whether of the thermo-setting or thermo-plastic type and especially synthetic resins such as phenol-formaldehyde condensation products, by dying or otherwise colouring the filler from an aqueous medium. A dyestuff and a filler may be selected which have a mutual affinity e.g. a direct cotton colour and wood meal. Alternatively an insoluble lake or pigment may be precipitated from aqueous solution upon and within the filler. An important feature of the invention consists in using vat dyes or sulphur dyes, but other dyes, and in particular the mordant dyes, can be used.

When we refer to dyeing or colouring the filler we do not include merely mixing the colouring matter with the filler. The colouring matter must impregnate the filler after the manner of dyeing although it is not essential that the colour should be fast to washing.

As indicated hereinbefore, the fillers may be coloured by several methods. They may in many cases be dyed in aqueous medium by means of water soluble dyestuffs such as the direct cotton colours and acid colours. Or they may be dyed with sulphur dyes or vat dyes which are afterwards developed by oxidation. They may also be coloured by the precipitation therein or thereon of an insoluble dye or colouring matter from aqueous solution. Thus a metallic or other lake of a water-soluble dyestuff or an azo dyestuff or an inorganic pigment may be precipitated or formed and precipitated upon or within the filler. The use of wetting-out agents in connection with the precipitation of an insoluble colouring matter is advantageous in securing adequate penetration of the filler by the solutions used. Finally a dyestuff may be adsorbed on to the filler from a colloidal dispersion of the dyestuff in an aqueous medium.

It is preferable to dye or otherwise colour the filler in absence of the plastic but if desired as already indicated this operation may be performed in presence of the plastic.

Different shades may in some cases be produced by mixing together suitable proportions of fillers which have previously been dyed or coloured differently. In all cases, however, it will be seen that the present invention avoids the necessity of mixing the colouring matter in solid form, with the filler and plastic. In some cases where the pigment in solid form is merely mixed with the plastic and filler and is thus present in a separate disperse phase in the moulded resin it is not adequately wetted by the plastic and the phenomenon known as "blooming" or "chalking" occurs. In the moulded articles produced by the present invention no separate disperse phase of pigment is present since this is distributed upon or within the filler and this disadvantage does not therefore arise. In this dispersed condition the colour is, in many cases, less susceptible to solvent action and less susceptible to bleeding than when incorporated in the usual way.

A further advantage of the present invention, in contrast to those processes in which the solid pigment is mixed with the filler and plastic, lies in the fact that the colour is more uniformly and adequately dispersed. It is probably for this reason that a smaller quantity of colouring matter is as a rule required to produce the desired shade.

When the plastic itself is coloured or liable to become coloured it may be necessary, in order to enable the filler to exhibit its colour, to incorporate in the moulding composition a hiding agent comprising a white pigment such as whiting, french chalk, lithopene, zinc oxide, titanium oxide or the like.

Mottled and multi-colour effects can be readily produced by the conjoint use of differently coloured or coloured and uncoloured fillers which are separately mixed with the plastic material and then juxtaposed as desired in the mould. By the use of suitable plastics transparent and opaque effects can be produced.

Dated this 7th day of April, 1933.

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12, Church Street, Liverpool, 1,
Chartered & Registered Patent Agents.

COMPLETE SPECIFICATION.

Improvements in and relating to the Manufacture of Coloured Moulding Compositions.

We, HAROLD CLAYTON, of 12, Broadway Avenue, Cheadle, in the County of Chester, and HARRY JONES, of 9, Vale Street, Heywood, near Manchester, in the

County of Lancaster, both British Subjects, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement :—

This invention relates to improvements in the manufacture of coloured moulding compositions.

It is customary in the manufacture of moulded articles to prepare a moulding composition comprising a mixture of a plastic, generally a synthetic plastic, and a filler and then to form shaped articles therefrom by moulding in a press preferably at an elevated temperature. Coloured articles are generally made by mixing with the plastic a proportion of finely divided pigment or other colouring matter during or after the incorporation of the filler.

It has been proposed to produce a moulding material composed of woven fabric impregnated with a fusible resinous binder and subdivided into substantially dry flakes of such size (e.g. from $\frac{1}{8}$ to $1\frac{1}{2}$ inches long by from $\frac{1}{8}$ to $1\frac{1}{2}$ inches wide) small enough to permit the moulding composition to flow in a mould under the influence of heat and pressure and large enough substantially to prevent the flakes sticking together in irregular masses after impregnation; it was also suggested to produce striking effects by dyeing part or all of the fabric pieces with various colours or by including pigments in the composition.

It has also been proposed to produce variegated colour effects by commingling a potentially reactive resin binder, for example of the phenol-aldehyde type, a filler and a colouring material the latter in the form of discrete particles, for instance loose aggregates of dyed wood fibre or of pigmented or dyed aggregates of any kind which are sufficiently fragile to be broken up or deformed by pressure, and then extruding the mixture into an elongated preformed mass.

There has also been proposed a manufacture of artificial materials containing fillers from condensation products made by condensing aromatic amines with formaldehyde in presence of acid, precipitating the condensation product by eliminating the acid and freeing the precipitated product from electrolytes wherein the filler is mixed with the condensation product whilst the latter is in a moist condition, before or after removal of the electrolytes, the mixture freed from electrolytes is dried, and then compressed at a raised temperature, if necessary after communication. It was suggested in connection with this process that as fillers various animal, vegetable or mineral materials might be used, either in the form of powder, such as wood-meal, asbestine, powdered leather or powdered cork or in fibrous form such as cotton, wood-pulp, sulphite cellulose, sulphate cellulose or soda-cellulose, saw-dust, old paper, rags, linen, jute, silk, wool or the like and that if desired the filler might be subjected to a suitable pre-treatment, such as a dyeing or colouring process.

Finally it has been proposed to make coloured rubber and the like by first preparing a pigment consisting of a suitably finely divided substratum, substantially insoluble in water, coated with a vat colouring matter, and then incorporating this in the rubber mix. Rubber, however, is not a synthetic resin capable of being moulded by heat and pressure. The moulding of rubber includes the step of vulcanisation and the problem therefore is complicated by the necessity of employing colouring matters which are resistant to the reagents and to the temperatures which are employed.

According to the present invention, the process for the manufacture of a moulding composition consists in dyeing or otherwise colouring a finely divided filler as hereinafter defined, by an aqueous medium, and then mixing the resulting coloured filler by the aid of heat and in substantial absence of water with undyed synthetic resin, of the kinds hereinafter defined, whereby the filler is impregnated by the synthetic resin. The dyeing or colouring of the filler may take place after the filler has been added to the synthetic resin provided that it is effected before the resin has had an opportunity of permeating and penetrating the filler to such an extent as to render it incapable of being penetrated by an aqueous medium and provided also that the water is substantially removed before the filler is finally mixed with the resin. The use of wetting-out agents is of importance in the dyeing or colouring of the filler although not essential for success.

By the expression "filler" we mean an organic or inorganic substance of fibrous or cellular structure characterised by the requisite degree of subdivision and capable of retaining a colouring agent which is applied thereto. The degree of subdivision is substantially less than one twenty-fifth of an inch and is of the order of one hundred and fiftieth of an inch. The expression does not therefore, include subdivided woven fabric nor does it include long fibres. Examples of suitable substances are wood flour, wood meal, and asbestos powder which are customarily

employed in moulding compositions. Preferably they are sufficiently finely divided to pass a 60 mesh sieve. The colouring agent which is applied to the filler may be retained owing to the affinity, physical or chemical, of the filler therefor, or alternatively the colouring agent may be simply deposited or formed upon or within the filler or absorbed thereby.

The expression "synthetic resin" means a fusible artificially prepared resinous material capable of being moulded by heat and pressure to form an object which is hard at ordinary temperatures; it does not, however, include the resins prepared by condensing aromatic amines with formaldehyde.

The synthetic resins are substantially waterfree intermediate condensation products of phenol-formaldehyde, urea-formaldyhyde, thiourea-formaldehyde, or the like resins, or vinyl resins (including styrol resins).

The resins named above when mixed with finely divided organic fillers such as wood meal, impregnate the individual particles of filler so completely that the resin forms a substantially continuous phase throughout the mass, a property which is of considerable value, when the moulded articles ultimately produced are used for insulating purposes or where a degree of transparency is required.

The dyeing or colouring of the filler from an aqueous medium results in important advantages in practice and increases the range of colouring matters which it is possible to employ. Many direct cotton colours, sulphur dyes, vat dyes and the like which it is difficult or impossible to use, at any rate with good result, by the customary methods of incorporation may be employed. Some of these, owing to their fastness to light, heat, acid and the like, form extremely valuable colouring matters to employ in moulded articles. Moreover, by dyeing or colouring the filler itself darker shades are as a rule obtained than when an equal amounts of the colouring matter is simply mixed with the filler and synthetic resin.

A valuable economy is thus often secured in addition to an improved result.

A dyestuff and a filler may be selected which have a mutual affinity e.g. a direct cotton colour and wood meal. Alternatively an insoluble lake or pigment may be precipitated from aqueous solution upon and within the filler. An important feature of the invention consists in using vat dyes or sulphur dyes, but other dyes, and in particular the mordant dyes, can be used.

When we refer to dyeing or colouring the filler we do not include merely mixing the colouring matter with the filler. The colouring matter must impregnate the filler after the manner of dyeing although it is not essential that the colour should be fast to washing. When we refer to dyeing or colouring from an aqueous medium we mean that the filler is brought into contact with an aqueous solution or suspension of colouring matter or colour-forming substance.

As indicated hereinbefore, the fillers may be coloured by several methods. One general method consists in causing them to absorb a colouring matter held in aqueous solution. They may in many cases be dyed from an aqueous medium by means of water soluble dyestuffs such as the direct cotton colours and acid colours. Or they may be dyed with sulphur dyes or vat dyes which are afterwards developed by oxidation. They may also be coloured by the precipitation therein or thereon of an insoluble dye or colouring matter from aqueous solution. Thus a metallic or other lake of a water-soluble dyestuff or an azo dyestuff or an inorganic pigment may be precipitated or formed and precipitated upon or within the filler. The use of wetting-out agents in connection with the precipitation of an insoluble colouring matter is advantageous in securing adequate penetration of the filler by the solutions used. Alternatively a dyestuff may be adsorbed on to the filler from a colloidal dispersion of the dyestuff in an aqueous medium.

It is preferable to dye or otherwise colour the filler in absence of the synthetic resin but if desired as already indicated this operation may be performed in presence of the synthetic resin.

Different shades may in some cases be produced by mixing together suitable proportions of dyed filler and undyed filler or of fillers which have previously been dyed or coloured differently. In all cases, however, it will be seen that the present invention avoids the necessity of mixing the colouring matter in solid form, with the filler and synthetic resin.

In some cases where the pigment in solid form is merely mixed with the synthetic resin and filler and is thus present in a separate disperse phase in the moulded resin it is not adequately wetted by the resin and the phenomenon known as "blooming" or "chalking" occurs. In the moulded articles produced by the present invention no separate disperse phase of pigment is present since this is distributed upon or within the filler and this disadvantage does not therefore arise. Distributed in this way the colour

is, in many cases, less susceptible to solvent action and less susceptible to bleeding than when incorporated in the usual way. Moreover the electrical properties of the moulded articles are improved by the absence of a disperse phase of colour.

A further advantage of the present invention in contrast to those processes in which the solid pigment is mixed with the filler and synthetic resin, lies in the fact the the colour is more uniformly and adequately dispersed. It is probably for this reason that a smaller quantity of colouring matter is as a rule required to produce the desired shade.

When the synthetic resin itself is coloured or liable to become coloured it may be necessary, in order to enable the filler to exhibit its colour, to incorporate in the moulding composition a hiding agent comprising a white pigment such as whiting, French chalk, lithophone, zinc oxide, titanium oxide or the like.

Mottled and multi-colour effects can be readily produced by the conjoint use of differently coloured or coloured and uncoloured fillers which are separately mixed with the synthetic resin and then juxtaposed as desired in the mould. By the use of suitable resins transparent and opaque effects can be produced.

The following examples 1 to 5 illustrate suitable methods of dyeing the filler.

EXAMPLE 1.

100 grams of wood meal (of about 90 mesh i.e. of maximum particle size about 0.15 mm.) are wet out with one litre of water. This forms a fluent mass to which is added :—

15 cm^3 of caustic soda solution (66° Tw. or 1.33 specific gravity).

1 gm. of hydrosulphite (concentrated powder) and 5—10 grams of the vat dyestuff caledon blue R.C. (Colour Index No. 1114) are then pasted up with water and vatted at 50° C. with :—

15 ccs. of Caustic soda solution (66° Tw. or 1.33 specific gravity), and

2—3 gms. of hydrosulphite (concentrated powder). The dyestuff solution is then added to the fluent mass containing the wood meal, the temperature of these two being 50° C. and the whole is subjected to agitation at this temperature for 1 hour. The wood meal is then filtered off and oxidised with acidified sodium bichromate solution. After thorough washing with cold water the wood meal is pressed and dried.

EXAMPLE 2.

100 grams of wood meal of about 90 mesh, are wet out with about one litre of water and to this mixture is added an aqueous solution of 2 grams of the direct cotton dyestuff diphenyl chlorine yellow F.F. (Colour Index No. 814). The dye bath is then agitated at an elevated temperature for ½—1 hour after which the wood meal is filtered off, washed, pressed and dried.

EXAMPLE 3.

100 grams of wood meal of about 90 mesh, are wet out with one litre of water and the mixture heated to 90° C. 5 grams of the sulphur dyestuff, eclipse blue B. (Colour Index No. 958), are dissolved in a solution of 10 grams of sodium sulphide crystals and 10 grams of sodium carbonate, at the boiling point. This colour solution is then added to the mixture containing wood meal and the whole subjected to agitation for 1 hour at 90° C. with an addition of 20 grams of sodium sulphate after ½ hour.

After dyeing the wood meal is filtered off, washed well and soaped at 50—70° C. It is then pressed and dried.

EXAMPLE 4.

100 grams of wood meal are wet out using one litre of water.

2 grams of a soluble or partially soluble acid dyestuff such as orange II (Colour Index No. 151) are wet out with one gram of Turkey red oil and dissolved in water. This is then added to the wood meal bath and the temperature raised to the boil during agitation. 4 grams of barium chloride (in solution) are then added to the bath and the boiling continued for 5 minutes. The coloured wood meal is later filtered off, washed with cold water pressed and dried out.

EXAMPLE 5.

The procedure described in example 4 is followed by employing asbestine, i.e. micro-asbestos instead of wood meal.

The preferred method of incorporating the dyed filler with the plastic is as follows :—

A fusible intermediate condensation product of a synthetic resin prepared in known manner is melted on heated rollers and there is incorporated therewith a proportion of dyed filler corresponding to that usually employed when using undyed filler. White pigment may be incorporated at this stage as well as a lubricant and any other additional ingredients which may be required. The mixing is then continued on the heated rollers until a uniform product is obtained. The product is then cooled, broken up and moulded with heat and pressure in the usual way.

The invention is not, of course, limited to the preferred forms described above which are given merely by way of illustration.

Having now particularly described and ascertained the nature of our said inven-

tion and in what manner the same is to be performed, we declare that what we claim is :—

1. Process for the manufacture of a moulding composition which consists in colouring finely divided filler of the kinds herein defined by an aqueous medium and then mixing the resulting coloured filler by the aid of heat and in substantial absence of water with undyed synthetic resin of the kinds herein defined whereby the filler is impregnated by the synthetic resin.

2. Process for the manufacture of a moulding composition as claimed in claim 1 in which the synthetic resin is of the thermo-setting type.

3. Process for the manufacture of a moulding composition as claimed in any of the preceding claims in which the filler is coloured by dyeing with a vat dye.

4. Process for the manufacture of a moulding composition as claimed in either claim 1 or 2 in which the filler is coloured from an aqueous medium with an insoluble pigment.

5. Process as claimed in claim 4 in which the colouring of the filler is effected in presence of a setting-out agent.

6. Process for the manufacture of a moulding composition as claimed in either of claim 1 or 2 in which the filler is coloured by dyeing with a sulphur dye.

7. A moulding powder comprising dyed finely divided filler of the kinds herein defined mixed and impregnated with synthetic resin of the kinds herein defined.

8. A moulding powder as claimed in claim 7 in which the filler is vat dyed.

9. A moulding powder as claimed in claim 7 in which the filler is sulphur dyed.

10 A moulding powder as claimed in any of claims 7 to 9 in which the filler is wood meal.

11. Coloured moulding compositions and process for their manufacture, substantially as described.

Dated this 26th day of February, 1934.

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Abingdon: Printed for His Majesty's Stationery Office, by Burgess & Son.
[Wt. 8012B.—50/8/1937.]